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United States Patent [19][11] **Patent Number:** **5,981,266****Srivastava et al.**[45] **Date of Patent:** ***Nov. 9, 1999**[54] **MICROBIAL PROCESS FOR THE MITIGATION OF SULFUR COMPOUNDS FROM NATURAL GAS**[75] Inventors: **Kailash C. Srivastava**, Centreville;
Daman S. Walia, Clifton, both of Va.[73] Assignee: **Gas Research Institute**, Chicago, Ill.

[*] Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

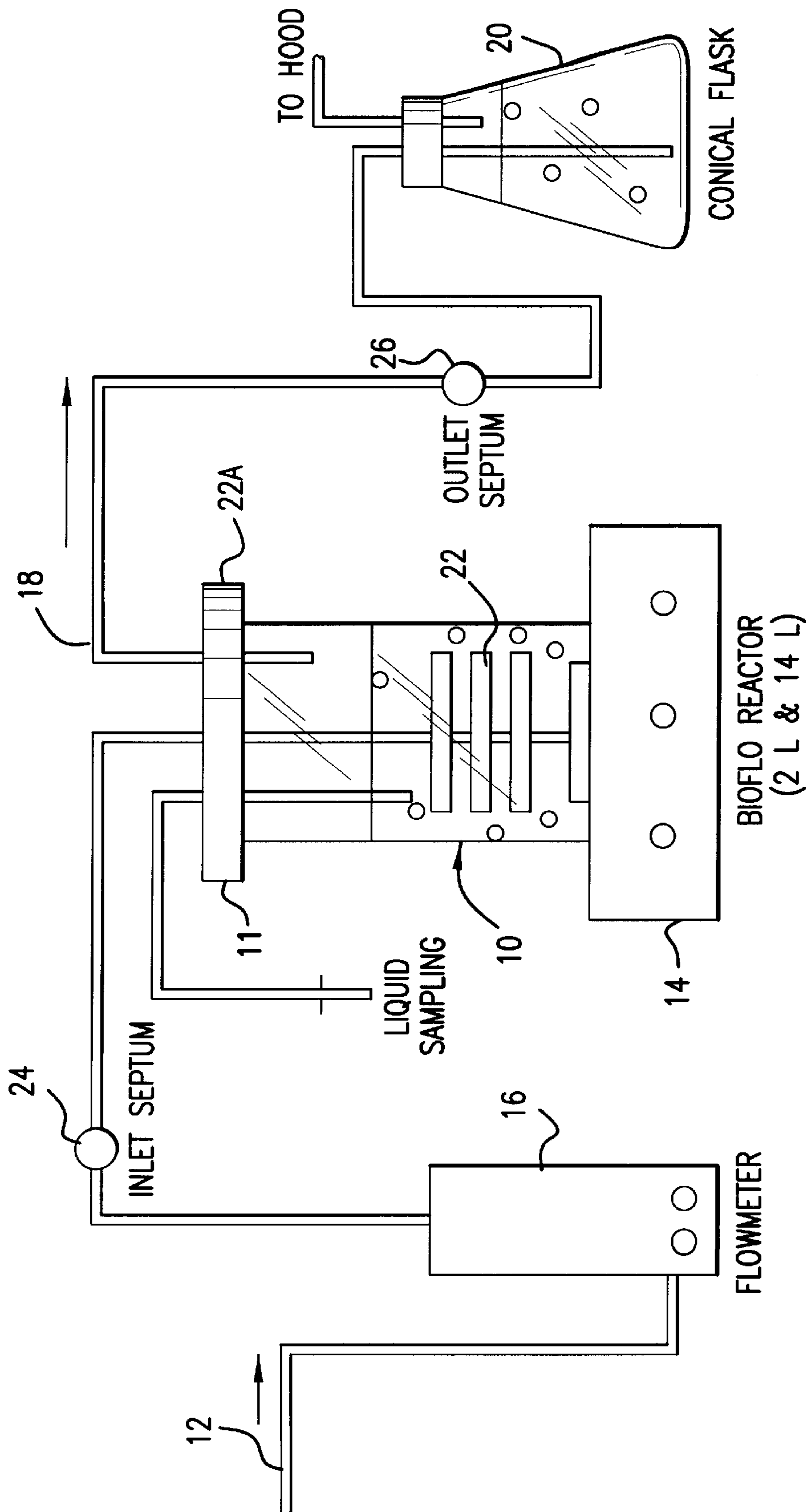
[21] Appl. No.: **08/651,793**[22] Filed: **May 20, 1996**[51] **Int. Cl.**⁶ **A61L 9/01**; C12N 1/00[52] **U.S. Cl.** **435/266**; 435/262; 435/822[58] **Field of Search** 435/266, 262,
435/822[56] **References Cited****U.S. PATENT DOCUMENTS**

1,701,825	2/1929	Seil	435/266
4,242,448	12/1980	Brown, III	435/42
4,666,852	5/1987	Cork	435/262
4,758,417	7/1988	van Lookerren-Campagne et al. .	423/ 231
4,760,027	7/1988	Sublette	435/266
4,880,542	11/1989	Sublette	210/611
4,931,262	6/1990	Sonta et al.	423/220
4,968,622	11/1990	Berzacy et al.	435/266
4,971,151	11/1990	Sheehy	166/246
5,044,435	9/1991	Sperl et al.	166/246
5,077,208	12/1991	Sublette	435/168
5,217,615	6/1993	Tyagi et al.	210/611
5,232,676	8/1993	Wolff et al.	423/210
5,236,677	8/1993	Torres-Cardona et al.	423/230
5,250,102	10/1993	Barnes et al.	75/710
5,297,625	3/1994	Premuzic et al.	166/246
5,354,545	10/1994	Buisman	423/242.1
5,385,842	1/1995	Weimer et al.	435/262

FOREIGN PATENT DOCUMENTS0218958A2 4/1987 European Pat. Off. .
0244659A2 11/1987 European Pat. Off. .**OTHER PUBLICATIONS**Aerobic Oxidation of Hydrogen Sulfide by Thiobacillus Denitrificans, K. Sublette, *Biotechnology and Bioengineering*, vol. XXIX, pp. 690–695, (1987).Biological Removal of H₂S From Sour Natural Gas, K. Srivastava, Oct. 1992 GRI Liquid Redox Sulfur Recovery Conference, pp. 129, 131–145.Optimization of Sulp[hur Production in a Biotechnological Sulphide-Removing Reactor, Buisman, et al., *Biotechnology and Bioengineering*, vol. 35, pp. 50–56, (1990).Microbial Control of the Production of Hydrogen Sulfide by Sulfate-Reducing Bacteria, Montgomery et al., *Biotechnology and Bioengineering*, vol. 35, pp. 533–539, (1990).Microbial Desulfurization of Gases, Sublette et al., *Biotechnology and Bioengineering Symp. No. 17* (1986), pp. 543–564.Microbial Reduction of Sulfur Dioxide with Pretreated Sewage Sludge and Elemental Hydrogen as Electron Donors, Deshmane, et al., *Applied Biochemistry and Biotechnology*, vol. 39/40, (1993), pp. 739–752.Microbial Removal of Sulfur Dioxide from a Gas Stream with Net Oxidation to Sulfate, Dasu et al., *Applied Biochemistry and Biotechnology*, vol. 20/21, (1989), pp. 207–220.Oxidation of Hydrogen Sulfide by Flocculated Thiobacillus Dentrificans in a Continuous Culture, *Biotechnology and Bioengineering*, vol. 37, (1991) pp. 497–504.Oxidation of Hydrogen Sulfide by Mixed Cultures of Thiobacillus Dentrificans and Heterotrophs, Sublette et al., *Biotechnology and Bioengineering*, vol. XXIX, (1987) 759–761.Oxidation of Hydrogen Sulfide by Thiobacilli, Cadenhead et al., *Biotechnology and Bioengineering*, vol. 35, (1990) pp. 1150–1154.Oxidation of Hydrogen Sulfide by Thiobacillus Dentrificans: Desulfurization of Natural Gas, *Biotechnology and Bioengineering*, vol. XXIX, (1987) pp. 249–257.Production of Microbial Biomass Protein from Autotrophic Fermentation of Hydrogen Sulfide, Sublette, *Biotechnology and Bioengineering*, vol. 32, (1988) pp. 408–409.Reduction of Sulfur Dioxide by Desulfovibrio Desulfuricans in Co-culture with Fermentative Heterotrophs, Dasu et al., *Biotechnology and Bioengineering*, vol. 34, (1989) pp. 405–409.Removal Kinetics of Hydrogen Sulfide, Methanethiol and Dimethyl Sulfide by Peat Biofilters, Hirai et al., *Journal of Fermentation and Bioengineering*, vol. 70, No. 5, (1990) 334–339.Immobilization of an Autotrophic Bacterium by Coculture with Floc-Forming Heterotrophs, Ongcharit, et al., *Biotechnology and Bioengineering*, vol. 33, (1989), pp. 1077–1080.Immobilization of Thiobacillus Denitrificans for the Oxidation of Hydrogen Sulfide in Sour Water, *Applied Biochemistry and Biotechnology*, vol. 20/21 (1989) pp. 675–686.Kinetics of Chemical and Biological Sulfide Oxidation in Aqueous Solutions, Buisman, et al. (1990). *(not included).
Biotechnological Process for Sulfide Removal with Sulfur Reclamation, Buisman, et al., *ACTA Biotechnology*, vol. 9, pp. 255–267, (1990). *(not included).*Primary Examiner*—Leon B. Lankford, Jr.*Assistant Examiner*—Christopher R. Tate*Attorney, Agent, or Firm*—Pauley Petersen Kinne & Fejer

[57]

ABSTRACTAn anaerobic process of desulfurizing a sour natural gas stream wherein a selected consortium of chemoautotrophic bacteria converts H₂S and other sulfur species into elemental sulfur, which is recovered as a product. The process is conducted at pressures of up to 1000 psi and temperatures up to 140° F. (10° C. to 60° C.), and mitigates up to 10,000 ppm H₂S to pipeline standards of ≤4 ppm and up to 10% CO₂ to ≤2% CO₂.**6 Claims, 9 Drawing Sheets**



EXPERIMENTAL SET-UP FOR THE 2 L AND 14 L REACTORS

FIG.1

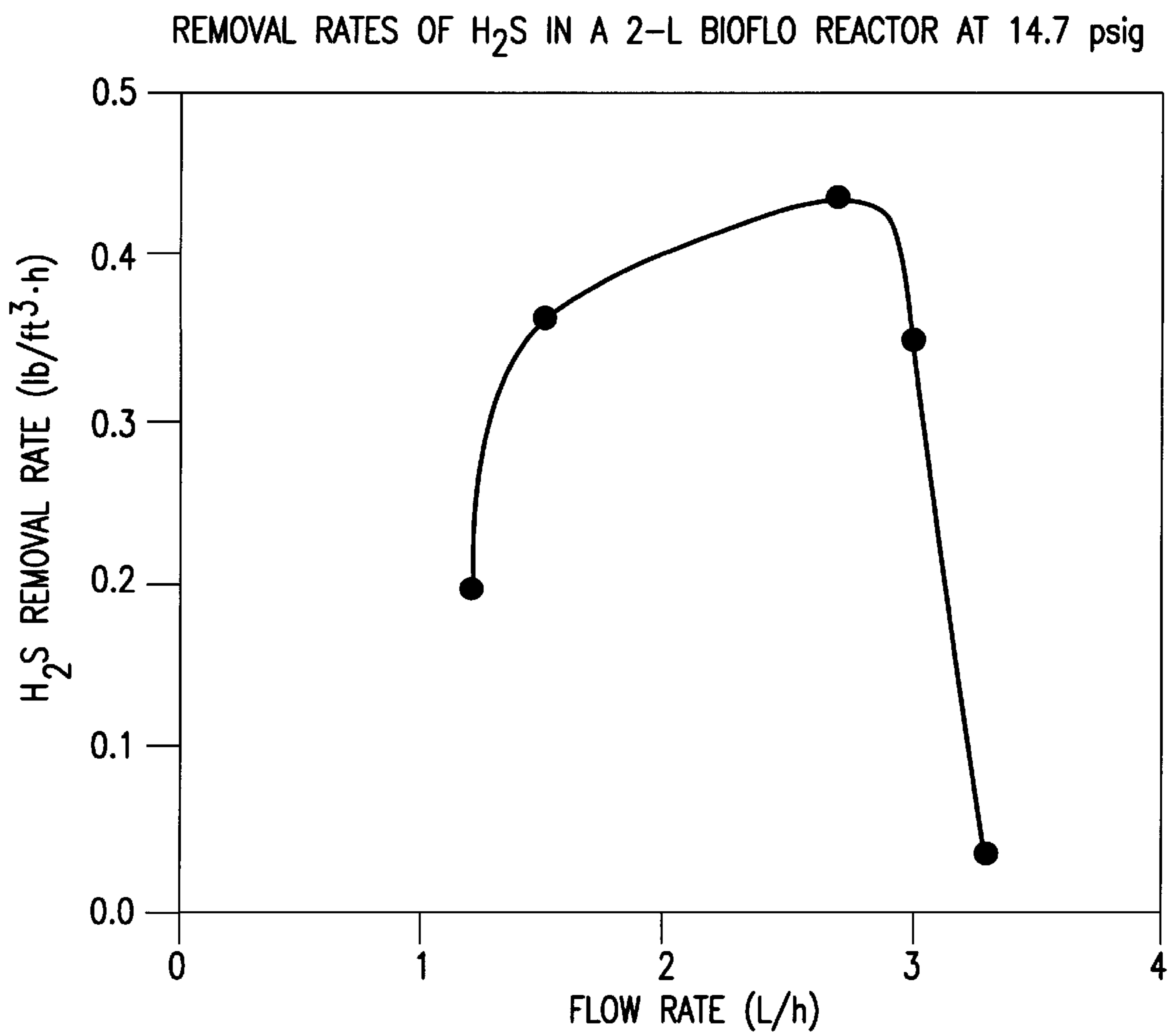
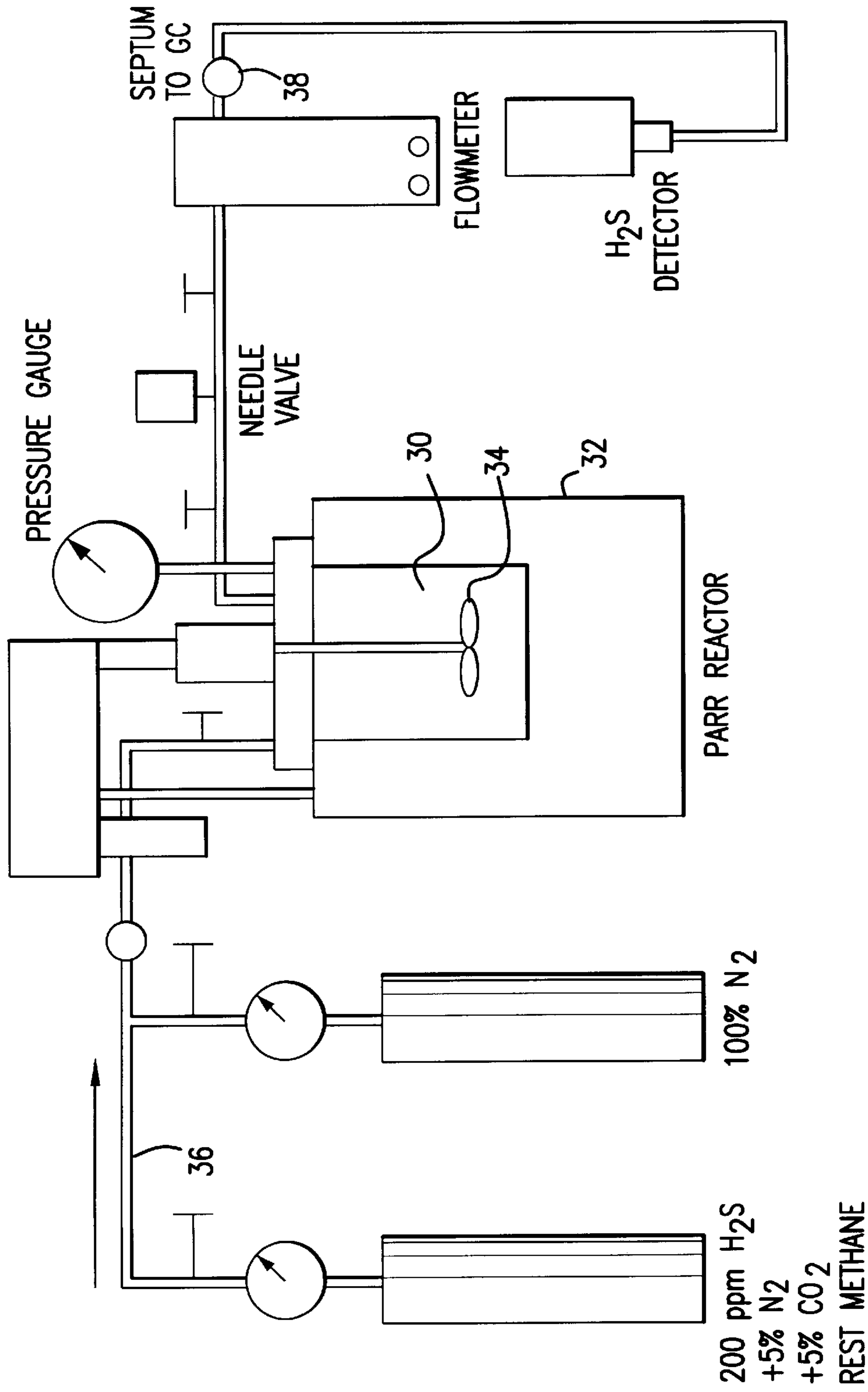
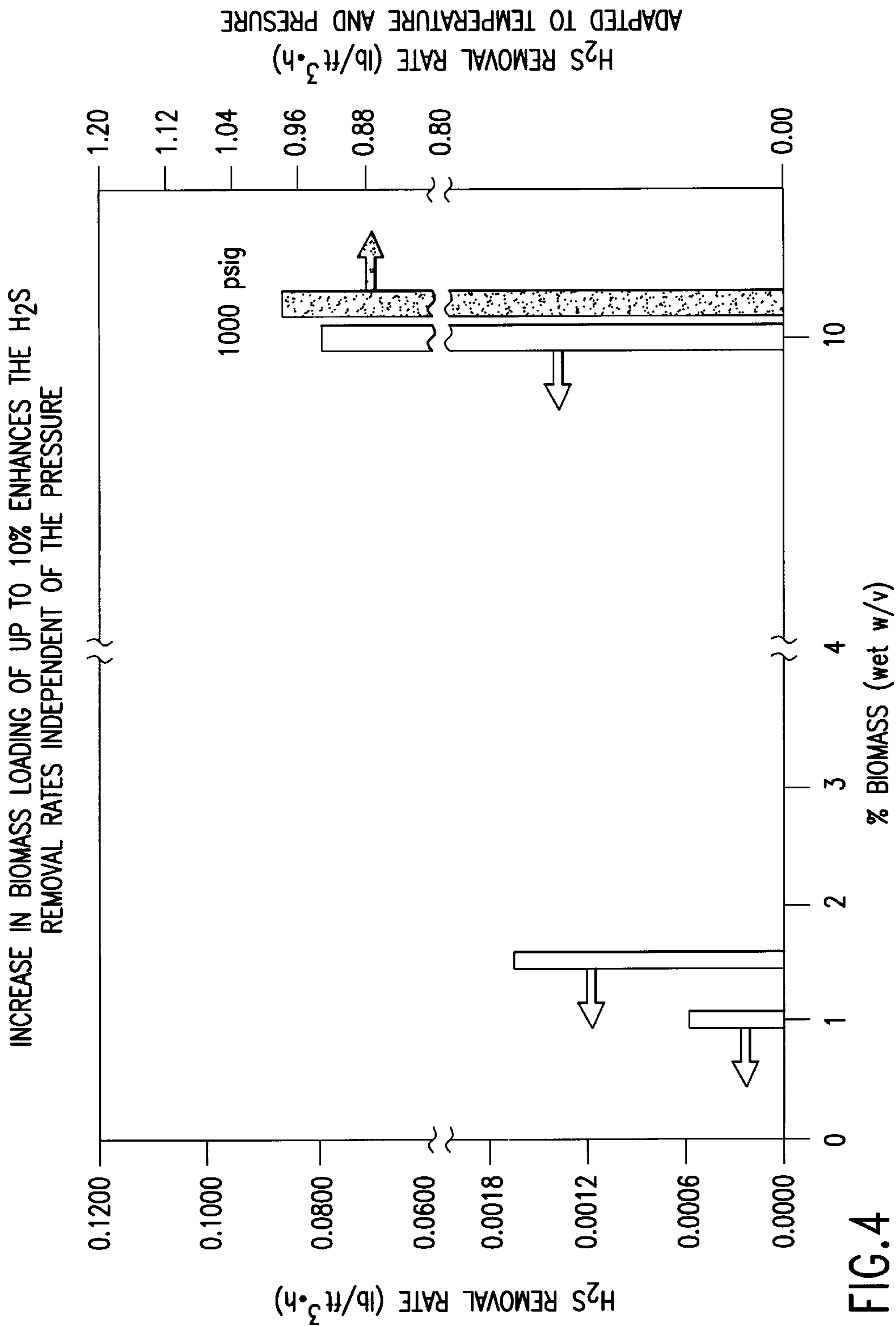


FIG.2



EXPERIMENTAL SET-UP FOR THE 1 L PARR PRESSURE REACTOR

FIG.3



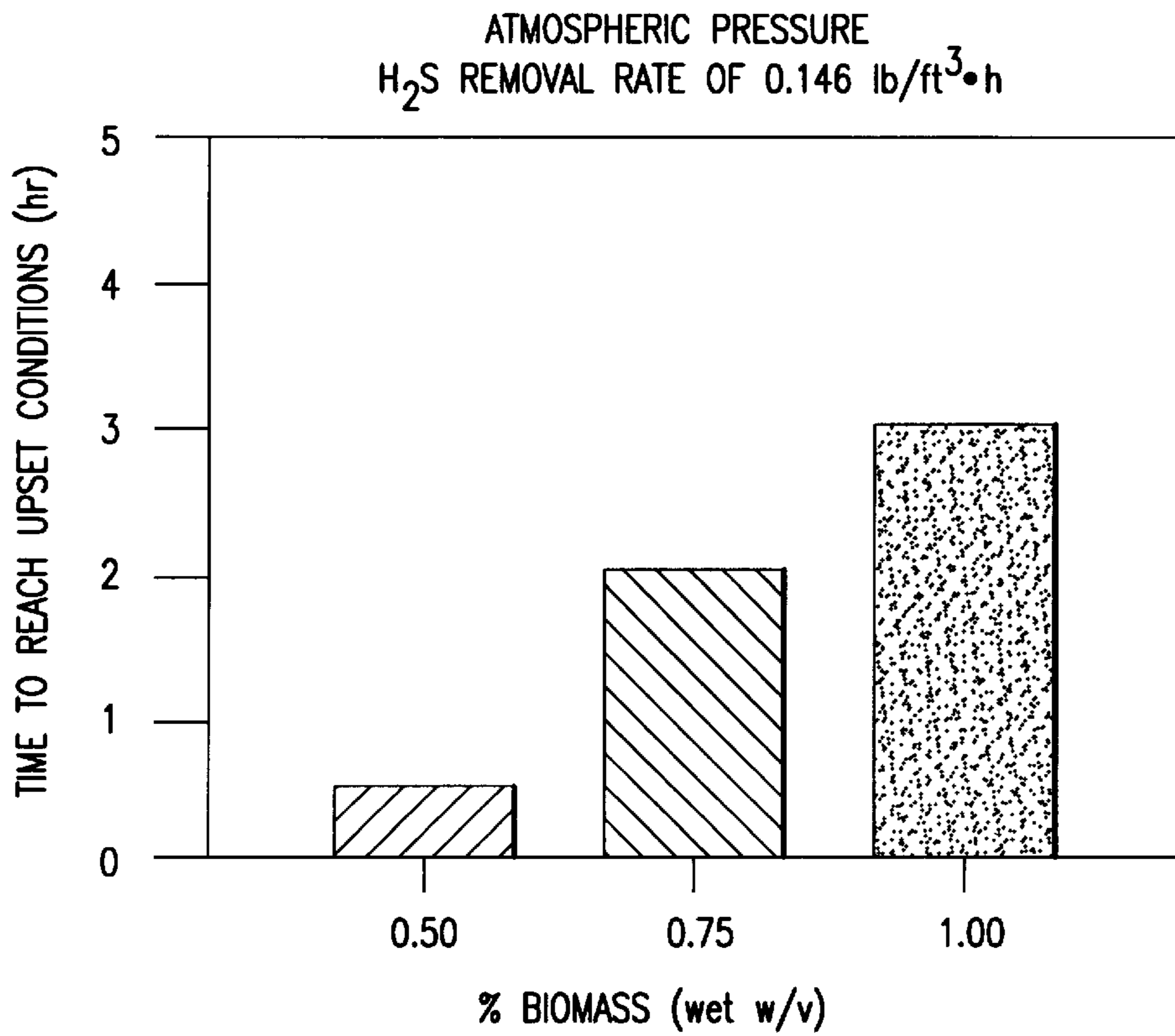


FIG.5

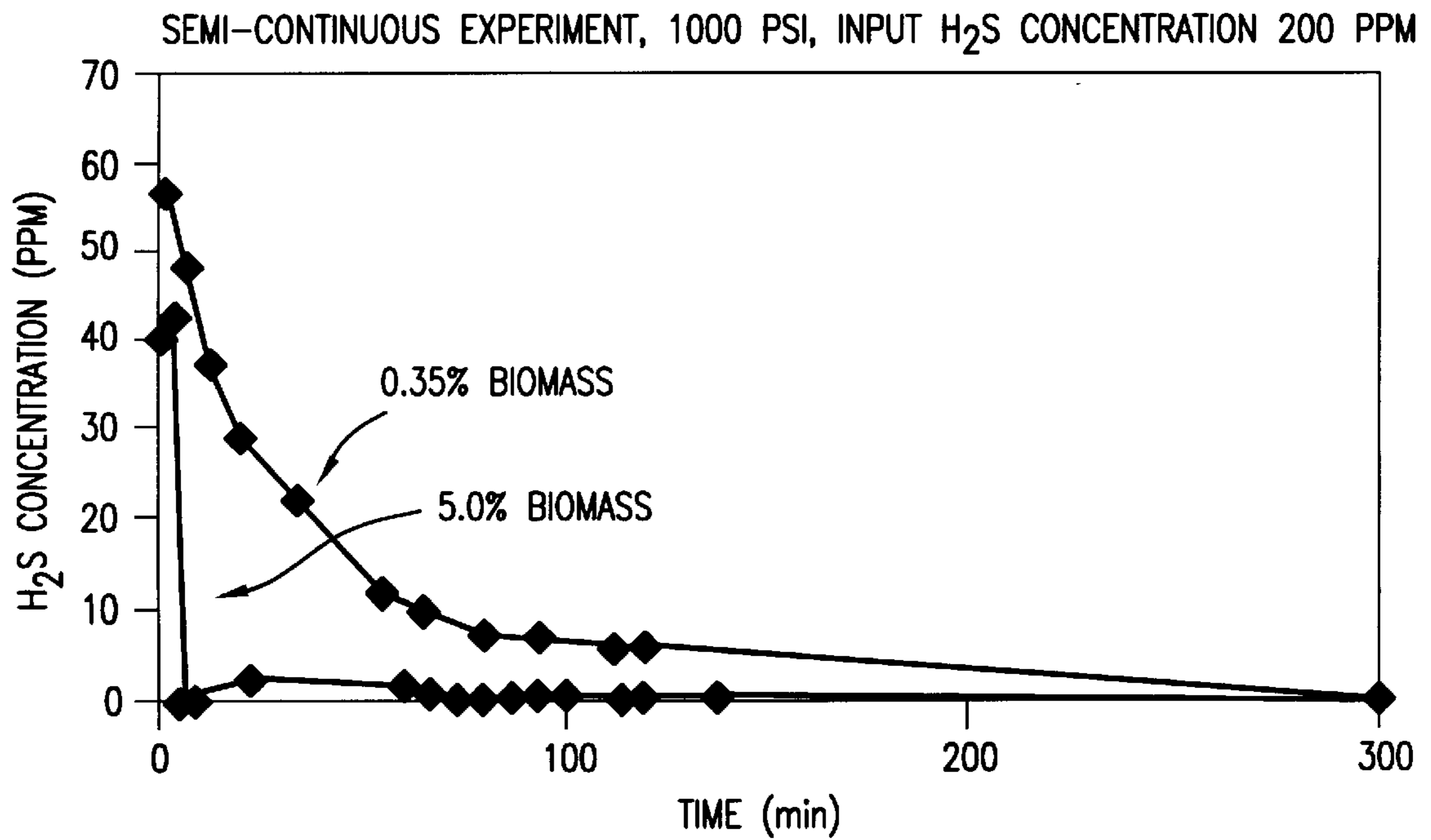


FIG.6

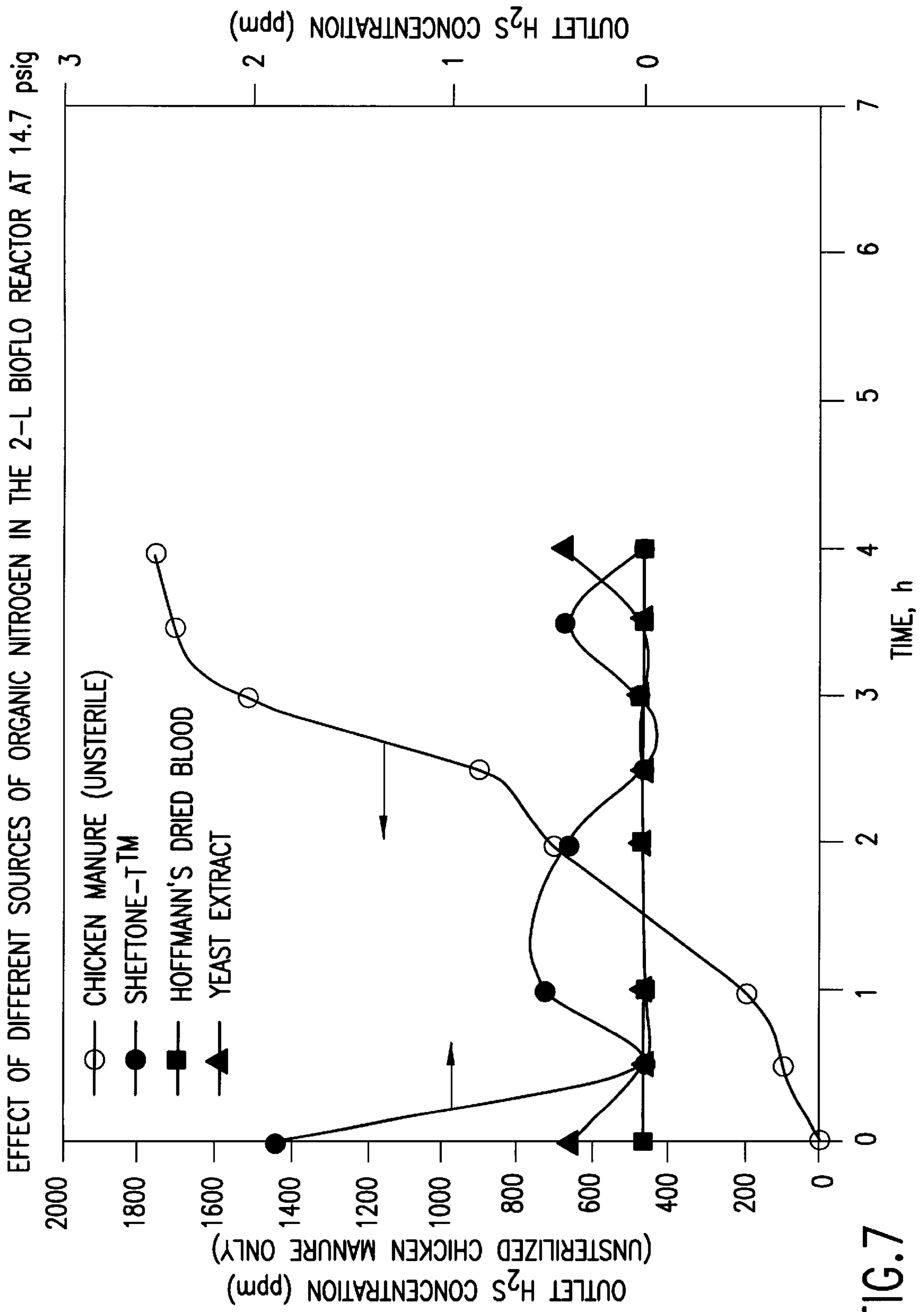


FIG. 7

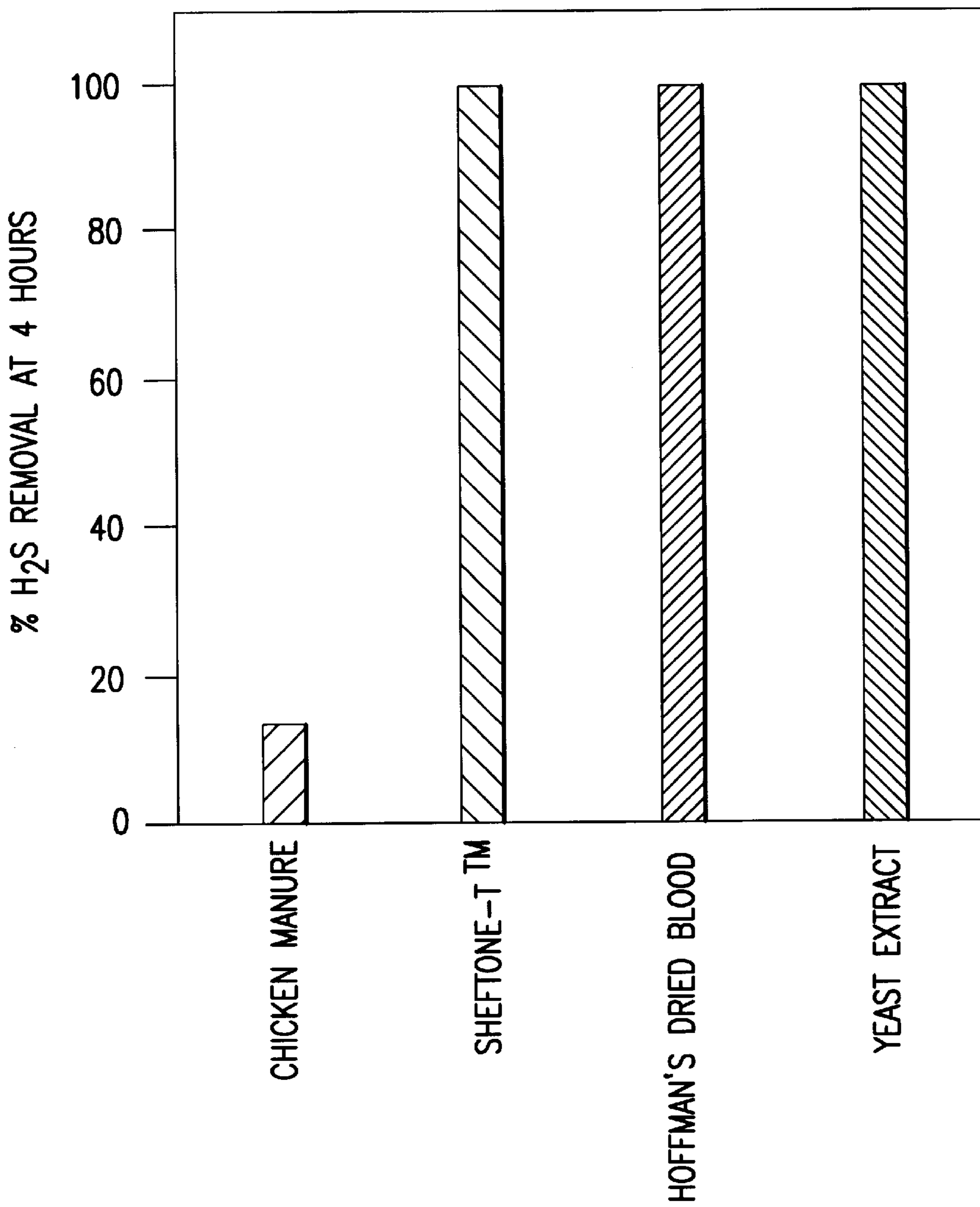


FIG.8

REMOVAL OF H₂S FROM A GAS COMPOSITION OF 10,000 ppm H₂S, 10% CO₂
IN N₂ IN A PARR PRESSURE REACTOR IN BATCH MODE AT 1000 psi
CONTAINING DIFFERENT SOURCES OF ORGANIC NITROGEN WITH 10% (WET W/V) SSII

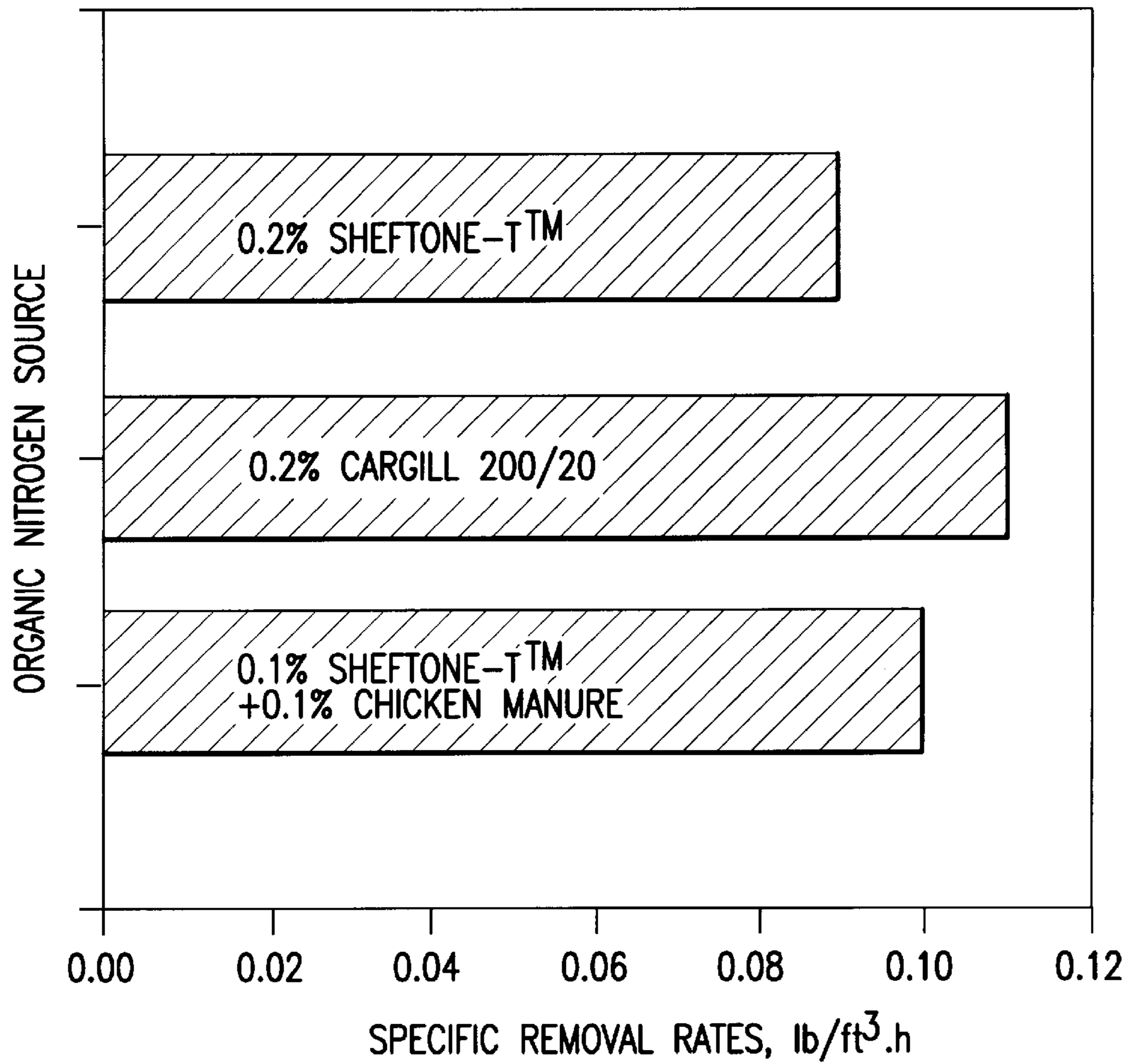


FIG.9

BIOCONVERSION OF H₂S TO ELEMENTAL SULFUR IN PARR PRESSURE REACTOR AT DIFFERENT TEMPERATURES BY AMCC CONSORTIUM SS11

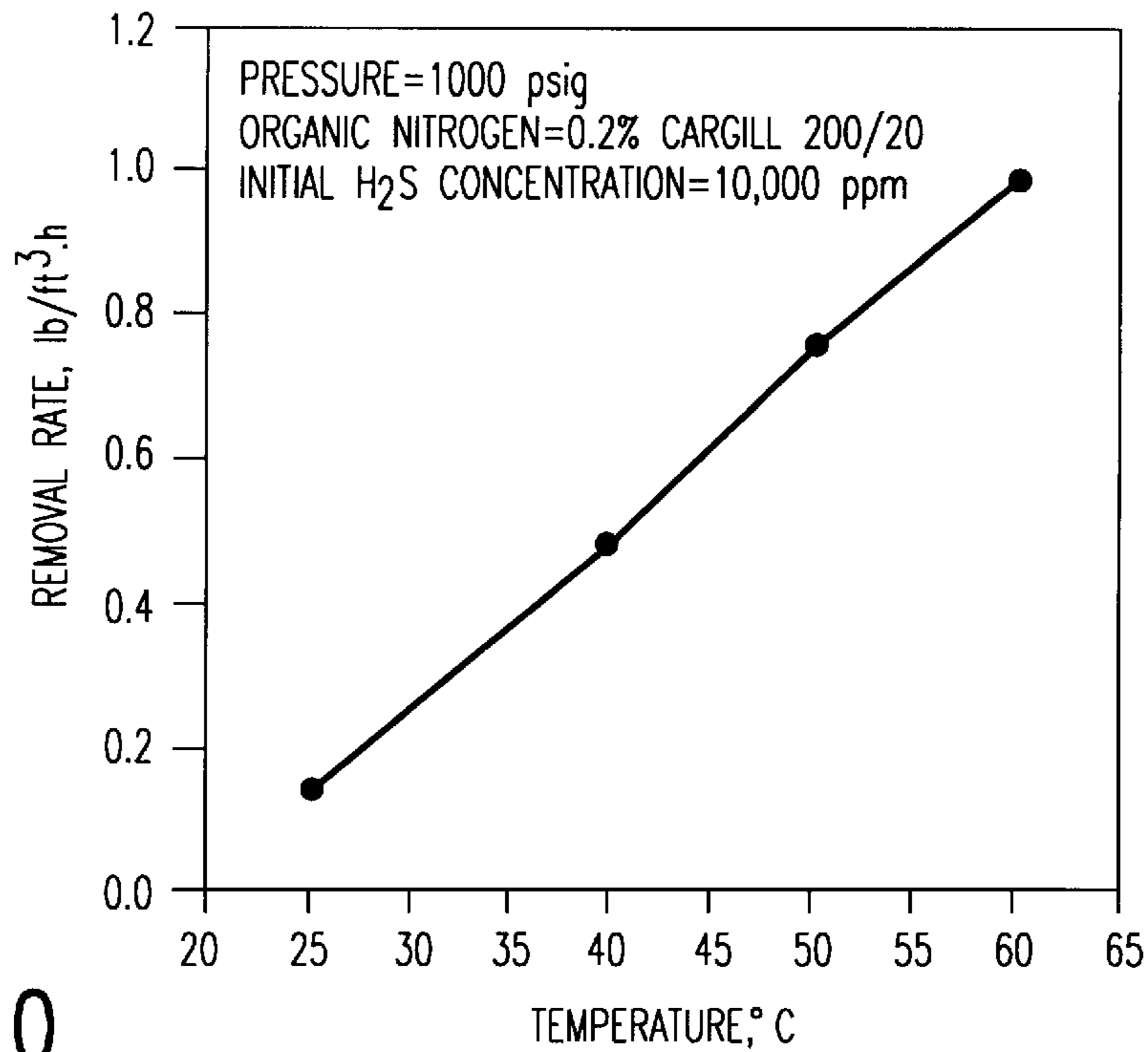


FIG.10

THE RATE OF REMOVAL OF CO₂ AT DIFFERENT TEMPERATURES IN 1-L PARR PRESSURE REACTOR WITH 10% SS11+0.2% CARGILL 200/20 AT 1000 psi

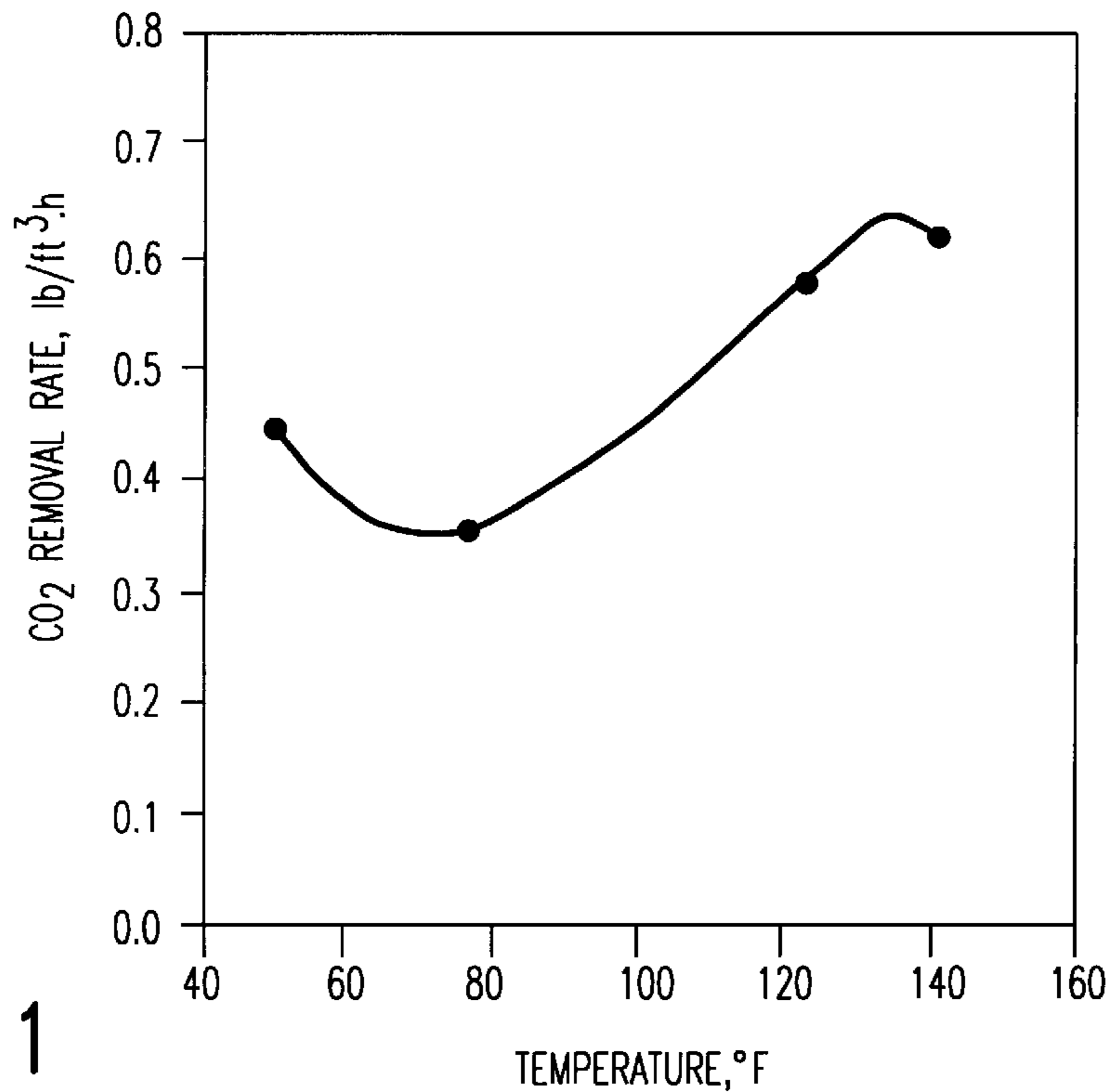


FIG.11

MICROBIAL PROCESS FOR THE MITIGATION OF SULFUR COMPOUNDS FROM NATURAL GAS

BACKGROUND OF THE INVENTION

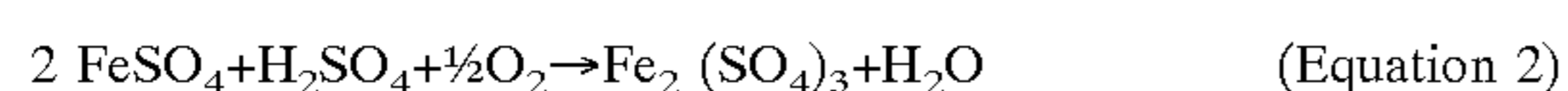
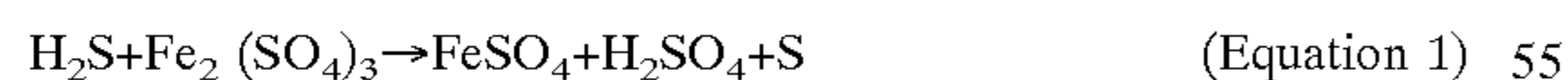
The present invention relates to a process for removing H₂S and other sulfur species under anaerobic conditions from sour gases. In particular, the present invention relates to the microbiological treatment of sour natural gas to remove H₂S and other sulfur species, such as carbon disulfide, methyl mercaptan, ethyl mercaptan and dimethyl sulfide, from the natural gas stream, and recover elemental sulfur as a product of the process.

Natural gas reserves in the U.S. often contain hydrogen sulfide (H₂S) as a major contaminant. Hydrogen sulfide is an acid gas that is toxic and corrosive in the presence of water. A significant portion of total gas production does not meet pipeline standards and needs treatment to reduce the H₂S concentration to ¼ grain per 100 standard cubic feet, or ≤4 ppm on a volume basis.

A commonly used commercial process for the removal of H₂S from the gas stream is the amine process, followed by the Claus process for sulfur recovery. In the amine process, the gas stream is contacted with the amine solvent to remove H₂S, then the amine solvent is heated to 90–150° C. (194–302° F.) to liberate H₂S and regenerate the solvent, which is recycled. Although the H₂S is removed from the natural gas stream, it still must be disposed of. Hydrogen sulfide generated during regeneration of the amine solvent can either be incinerated, which converts the hydrogen sulfide disposal problem into an air pollution problem due to the production of SO₂, or treated by physicochemical methods such as the Claus process. In the Claus process, H₂S is fed into a reaction furnace, and the reaction gas is passed through a series of catalytic reactors to convert the H₂S into elemental sulfur. Although the Claus process produces a high quality elemental sulfur product, the process is often too expensive for small capacity plants (of less than 2 MM SCF/d).

Several microbiological methods have been investigated for the treatment of gas streams containing sulfides. In one process, the anaerobic photosynthetic bacterium *Chlorobium thiosulfatophilum* is used to convert sulfides to sulfate. Cork, D. J. and Ma, S. "Acid-Gas Bioconversion Favors Sulfur Production", Biotech. and Bioeng. Symp. No. 12, 285–290 (1982).

In another process, which is the basis for a process known as Bio-SR, the Fe⁺² formed during H₂S oxidation in accordance with Equation (1), is converted to Fe⁺³ by the bacterium *Thiobacillus ferrooxidans* in accordance with Equation (2).



A number of bacteria (called chemoautotrophic) use reduced sulfur compounds as a source of energy, CO₂ or bicarbonate as a source of carbon, and NH₄⁺ as a source of reduced nitrogen. *Thiobacillus denitrificans* is one such organism. One process for the desulfurization of gas using *Thiobacillus denitrificans* is disclosed in Sublette, U.S. Pat. No. 4,760,027. That patent describes a process wherein bacteria of the *Thiobacillus* genus convert sulfides to sulfates under aerobic conditions and at a controlled temperature of about 30° C.

Most of the studies on H₂S removal have been performed under aerobic conditions and at H₂S concentrations of <1000 ppm. Such methods, however, cannot be used for the direct removal of H₂S from sour natural gas because of the potential danger of explosion when methane and air are mixed.

The process of the present invention overcomes these limitations and problems of prior art H₂S removal processes because the process is carried out under anaerobic conditions. The process is known to be effective for treatment of inlet H₂S concentrations of up to 10,000 ppm (1%), at a pressure of 1,000 psi and at temperatures common to those required by the gas industry (e.g. 140° F., 60° C.). In addition, the process of the present invention reduces CO₂ levels of from 5% to 10% down to 2%.

In earlier research, ARCTECH developed a microbial consortium, SSII, from ARCTECH'S Microbial Culture collection (AMCC) to reduce the H₂S concentrations of up to 10,000 ppm to pipeline specifications of ≤4 ppm. The biological and physiological characteristics of this consortium and technical feasibility of the consortium to mitigate 1% H₂S to ≤4 ppm are the subject of a separate patent application. The information from laboratory scale bioreactor experiments using SSII served as the basis for further research, which is the subject of the present invention. The preliminary data from the laboratory scale bioreactor experiments was presented at the 1992 GRI Liquid Redox Sulfur Recovery Conference, Austin, Tex. on Oct. 4–6, 1992, by K. C. Srivastava, and entitled "Biological Removal of H₂S From Sour Natural Gas", which paper is hereby incorporated by reference in its entirety. The results from this preliminary work provided the experimental proof of the concept of biological H₂S removal under anaerobic conditions on bench scale. Nevertheless, additional scaled-up processing information was necessary for delineating the process parameters.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method of desulfurizing sour natural gas by microbiological techniques under anaerobic conditions, and recovering elemental sulfur as a product.

Another object of the present invention is to mitigate H₂S, other sulfur species, namely methyl mercaptan, ethyl mercaptan, dimethyl sulfide, and carbon disulfide, as well as carbon dioxide, in sour natural gas.

A further object of the present invention is to provide a low cost, economical and efficient process for the removal of H₂S from natural gas so that the gas meets pipeline standards of ≤4 ppm H₂S.

These and other objects are accomplished by a process in which a consortium of chemoautotrophic bacteria converts H₂S and other sulfur species into elemental sulfur, which is recovered as a product. More particularly, the invention involves the use of the consortium under anaerobic conditions and at pressures of up to about 1000 psi and temperatures in the range of 50° F. to 140° F. (10° C. to 60° C.) to oxidize sulfur species such as H₂S to elemental sulfur. In one embodiment of the invention, the process is carried out in a Pressure Reactor at pressures of about 1000 psi. The process of the invention is particularly suited for the removal of sulfide species from natural gas, although it may also be used to mitigate H₂S in geothermal vent gas, enhanced oil recovery vent gas, off-gas streams in the chemical industry, landfill gas, and biogas. Other reaction conditions contemplated here are described below.

The present invention may be better understood by reference to the accompanying drawings in conjunction with the following description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram illustrating the process of the invention in a reactor at atmospheric pressure.

FIG. 2 is a graph illustrating H₂S removal rates in the reactor of FIG. 1.

FIG. 3 is a flow diagram of the pressure reactor used in a preferred embodiment of the invention.

FIGS. 4 and 5 are graphs illustrating the effect of cell density on H₂S removal rates.

FIG. 6 is a graph illustrating the effect of biomass amount on the amount of time required to oxidize H₂S.

FIGS. 7 and 8 are graphs illustrating the effect of different nitrogen sources in the reactor of FIG. 1.

FIG. 9 is a graph illustrating the effect of different nitrogen sources in the reactor of FIG. 3.

FIG. 10 is a graph illustrating H₂S conversion in the pressure reactor system of FIG. 3.

FIG. 11 is a graph illustrating the effect of temperature on the rate of removal of CO₂ in the pressure reactor system of FIG. 3.

The microbiological consortium (hereinafter referred to as SSII) used in connection with the process of the present invention has been deposited in the American Type Culture Collection ATCC# (to be provided). This deposit was made by ARCTECH, Inc., on Oct. 6, 1998 with the ATCC Patent Depository and was acknowledged under the title, "Consortium SSII Sewage Sludge & Acid Mine Water Culture." Ms. Barbara M. Hailey of the ATCC informed Applicants that the ATCC Number for the deposit is ATCC 202177. The consortium comprises at least four morphologically distinct microbes.

The present invention may be carried out under any suitable conditions, the details of which can readily be ascertained by one skilled in this field in view of the present disclosure. Several non-limiting examples of suitable conditions follow.

Any suitable reactor can be used. Two examples are the reactors of FIGS. 1 and 3 as further described below.

The pressure of the sour gas stream can vary widely, without departing from the present invention. Atmospheric pressure and elevated pressures are specifically contemplated, though a sub-atmospheric pressure could also be used within the scope of the present invention. An elevated pressure from about 75 psi (52 N/cm²) to a pressure of or exceeding about 1000 psi (700 N/cm²) is specifically contemplated herein.

The reactor vessel may be maintained at any suitable temperature, for example, a temperature range of from about 50° F. to about 140° F. (10° C. to about 60° C.).

H₂S can be present in the sour gas stream at any suitable concentration, for example, from a nominal concentration to about 10,000 ppm. Optionally, the concentration of H₂S can be more than about 200 ppm, optionally more than about 5,000 ppm. The concentration can also vary within the scope of the invention.

The reactor vessel can contain from about 0.35% to about 10% biomass, or alternately at least about 5% biomass. Any suitable concentration of the biomass can be used, within the scope of the present invention.

The reactor vessel is desirably charged with an organic source of nitrogen. This may be done prior to pressurization or at other times, within the scope of the present invention.

The sour gas or other input gas stream which can be processed according to the present invention can contain hydrogen sulfide or other sulfur compounds. For example, any one or more of the following compounds may be present, and can be removed from the input gas stream by carrying out the present invention: H₂S, CH₃SH, C₂H₅SH, (CH₃)₂S, CS₂, or mixtures of any two or more of the foregoing species.

The input stream can also contain carbon dioxide, which the consortium according to the present invention can remove from the feed gas when the present invention is carried out under suitable conditions. For example, the input gas stream can contain from a nominal amount, alternatively at least about 5% by volume, to a larger amount, for example about 10% or more by volume, carbon dioxide. The consortium according to the present invention can, under suitable conditions, reduce the carbon dioxide content of the feed stream substantially, such as from a higher amount to less than about 2% by volume.

EXAMPLES

The following are several working examples illustrating how the present invention can be carried out. The scope of the invention is not limited in any way by the specific apparatus, conditions, and other details set out in the examples.

The SSII (ATCC—) used in connection with the present invention was cultivated in serum vials of 125 milliliter capacity under anaerobic conditions according to Srivastava, 1992. The serum vial contained 50 milliliters of the culture medium described in Table 1. The headspace of the vials was exchanged with an oxygen (O₂)-free mixture (80.20) of nitrogen (N₂), and carbon dioxide (CO₂). Vials were stoppered with butyl rubber stoppers and aluminum crimp sealed. The vials were then steam sterilized at 120° C. and 15 psi. Subsequently, the cooled vials were inoculated with 20% (w/o) of a previously cultivated culture of SSII. After 24 hours of cultivation at 68° F. (20° C.), the culture was inoculated in Wheaton bottles of 1 liter capacity containing 500 milliliters of culture medium (Table 1) and the bottles were prepared as described for the serum vials. The consortium was transferred into a maintenance medium having the composition set forth in Table 1. The SSII consortium and its medium were then used in the following experiments which illustrate the process of the present invention.

TABLE 1

Composition Of The Medium Component	
Medium Component	Quantity (g/L)
Disodium phosphate (Na ₂ HPO ₄)	1.20
Potassium phosphate (KH ₂ PO ₄)	1.80
Magnesium sulfate (MgSO ₄ 7 H ₂ O)	0.40
Ammonium chloride (NH ₄ Cl)	0.50
Calcium chloride (CaCl ₂)	0.03
Manganese sulfate (MnSO ₄ 7H ₂ O)	0.40
Ferric chloride (FeCl ₃)	0.02
Sodium bicarbonate (NaHCO ₃)	1.00
Potassium nitrate (KNO ₃)	5.00
Sodium thiosulfate (Na ₂ S ₂ O ₃)	10.00
Trace metal solution	15 mL

TABLE 1-continued

Composition Of The Medium Component	
	Quantity (g/L)
<u>Trace Metal Solution Component</u>	
EDTA	5.0
Zinc sulfate (ZnSO ₄)	2.2
Calcium chloride (CaCl ₂)	0.554
Manganese chloride (MnCl ₂)	0.506
Ferrous sulfate (FeSO ₄ ·7H ₂ O)	0.110
Ammonium molybdate (NH ₄ MoO ₄)	0.157
Cuprous sulfate (CuSO ₄)	0.157
Cobalt Chloride (CoCl ₂)	0.161
Water	100 mL

The experimental set-up for the following Experiments 1–4 is illustrated in FIG. 1. For each of these experiments, a liquid sample containing the SSII in its culture medium is loaded into a reactor 10, such as a BioFlo Reactor obtained from New Brunswick Scientific Co. The reactor 10 is then sealed with a stainless steel flange top 11. A simulated gas to be desulfurized is routed via line 12 into the reactor through a sparger 14 at the bottom of the reactor. A flowmeter 16, such as a Brooks flowmeter, is used to measure the flow rate of the simulated gas being passed into the reactor. The treated gas from the reactor is passed via line 18 through a sealed erlenmeyer flask 20 filled with water, with outlet connections to a fumehood (not shown). Bubbles in the flask downstream from the reactor indicate that the connections are leak proof. The reactor is also equipped with an agitator 22 in order to maintain the consortium in suspension. The gas concentrations of the synthetic gas entering and exiting the reactor 10 are determined from samples obtained via an inlet septum 24 and an outlet septum 26, respectively.

Experiment 1

One liter of the SSII in the culture medium described in Table 1 was transferred to a 2 liter capacity BioFlo reactor jar. Five milliliters of 10% Sheftone-T™, an organic nitrogen source obtained from Sheffields Products of Detroit, Mich., and 5 milliliters of 5% sodium thiosulfate were aseptically added to the reactor jar. The reactor vessel was then sealed with a stainless steel flange top. (See 11 of FIG. 1). The contents of the reactor were then stirred for 30 minutes.

A simulated sour natural gas (SNG) stream consisting of 5,000 ppm H₂S, 10.1% CO₂, 11.6% N₂ and 77.29% CH₄ was sparged at a rate of 1.2 liters per hour. The pH of the culture medium (Table 1) and the optical density (absorbance at 460 nm OD₄₆₀) of the liquid containing the SSII consortium were 7.5 and 0.63, respectively, at the start of the experiment. This optical density corresponded to a cell population of 10⁶ cells/mL. The inlet and outlet gas concentrations were measured as a function of time and are recorded in Table 2 below:

TABLE 2

Time, (Hours)	Inlet H ₂ S Concentration (ppm)	Outlet H ₂ S Concentration (ppm)
0	5905	0.65
1.0	5905	1.020
2.0	5454	3.16
3.0	5931	2.50

TABLE 2-continued

Time, (Hours)	Inlet H ₂ S Concentration (ppm)	Outlet H ₂ S Concentration (ppm)
4.0	5551	2.26
5.5	4620	1.014
6.0	5495	2.14
7.0	5781	2.91

The flow of the gas was stopped and the pH and OD₄₆₀ of the SSII suspension in the broth were 7.30 and 1.03, respectively. The SSII suspension was filtered with Whatman No. 1 filter paper to separate the larger suspended particles from the bacterial cells (SSII). Product analysis of the solid material indicated that the major product recovered was elemental sulfur. Then the liquid (filtrate) was centrifuged at 5,000 rpm×g to recover the cells of SSII from the liquid.

Experiment 2

A volume of 1.3 liters of the SSII in the culture medium of Table 1 was transferred to a 2 liter capacity BioFlo Reactor vessel. Similar to Experiment 1, a five milliliter suspension of 10% Sheftone-T™, and 5 milliliters of a 5% solution of sodium thiosulfate were added. The contents of the reactor vessel were agitated for one-half hour. A simulated sour natural gas stream containing 987 ppm of carbonyl sulfide (COS), 5029 ppm of H₂S, 996 ppm of methyl mercaptan (CH₃SH), 999 pm of ethyl mercaptan (C₂H₅SH), 1001 ppm of dimethyl sulfide ((CH₃)₂S), 999 ppm of carbon disulfide (CS₂), 5% carbon dioxide (CO₂), 5% nitrogen (N₂) and the balance methane (CH₄) was sparged into the reactor at a rate of 1.2 L/h. The initial OD₄₆₀ and the pH of the SSII suspension were 1.57 and 8.12, respectively. The final OD₄₆₀ and pH at the end of the experiment were 3.3 and 6.74, respectively. Removal rates in terms of percentage removed were determined as a function of time and are recorded in Table 3 below:

TABLE 3

Time, (Hours)	H ₂ S % Removed	CH ₃ SH % Removed	C ₂ H ₅ SH % Removed	(CH ₃) ₂ S % Removed	CS ₂ % Removed
0	84.48	94.48	53.59	28.39	38.85
1	95.40	95.40	97.75	83.68	66.20
2	95.18	99.14	98.13	84.47	56.23
3	94.51	99.19	98.40	79.91	46.08

The results of this experiment demonstrate that the SSII can remove not only H₂S from sour natural gas, but other sulfur species as well.

Experiment 3

Experiment 1 was repeated except that the gas flow rate used in the process was varied. The specific oxidation rates in terms of sulfur removed as lbs/ft³/hr were determined as a function of the gas flow rate and are shown in FIG. 2.

The results of this experiment demonstrate that the oxidation rate increases as the gas flow rate increases up to a limit of 2.7 L/h. Gas flow rates greater than 2.7 L/h resulted in a rapid decline of the specific oxidation rate. This is not a limitation of the SSII but of the reactor capacity. In order to test this hypothesis, experiment 4 was conducted.

Experiment 4

A volume of 12 liters of the SSII consortium in the culture medium of Table 1 was transferred to a 14 liter capacity

reactor. A 100 milliliter volume of 8% Sheftone-T™ and 30 milliliters of 20% Sodium and Potassium phosphates were added to the reactor. The contents of the reactor were stirred constantly. A simulated natural gas stream containing H₂S was sparged into the reactor at 8.64 L/h. The gas composition was 5% carbon dioxide, 5% nitrogen, 1% hydrogen sulfide, and the balance methane. The initial pH and OD₄₆₀ were 7.4 and 2.70, respectively. The inlet and outlet gas concentrations were measured as a function of time and are recorded in Table 4 below:

TABLE 4

Time, (Hours)	Inlet H ₂ S Concentration (ppm)	Outlet H ₂ S Concentration (ppm)
0	3207	0
1	3217	0
3	3060	0
4	3286	0
5	3281	0
6	3290	0
7	3288	0

Thus, the experiment showed that the hypothesis is correct.

The experimental set-up for the following Experiments 5–8 and 10–12 is illustrated in FIG. 3.

For these experiments, a liquid sample containing the SSII consortium in its culture medium is loaded into a pressure reactor 30, such as a Parr pressure reactor. The pressure reactor is made of stainless steel and is housed in a metallic shell 32. The reactor can be pressurized up to 2000 psi. An agitator 34 is provided inside the reactor to maintain the SSII consortium in suspension. A simulated sour natural gas to be desulfurized is introduced into the reactor via inlet line 36. Periodic gas samples from the head space of the reactor are withdrawn through a septum 38 so that progress of the desulfurization process can be monitored.

Experiment 5

Six hundred milliliters of SSII in the culture medium of Table 1 are charged into the pressure reactor after adding 10 milliliters each of 5% Sheftone-T™ and 5% sodium thio-sulfate. The initial pH and OD₄₆₀ of the culture broth are 8.16 and 1.66, respectively. The reactor is pressurized to 1000 psi with a sour gas stream containing 5000 ppm H₂S. The agitator is started, and the gas concentration in the head space is monitored at particular intervals of time by withdrawing gas samples through the septum. The readings are noted as a function of time and are recorded in Table 5 below:

TABLE 5

Time (Hours)	H ₂ S Concentration (ppm)
0	1744
1	1680
3	1609
5	1566
20	1146
23	921
25	442
26.5	191
26.75	0.25

When the H₂S is mitigated, the pressure is released and the pH and optical density of the liquid sample are measured. The liquid sample has a pH of 6.40 and an optical density of 3.26. The results of this experiment demonstrate that the SSII consortium can remove H₂S to meet regulatory

pipeline standards even at a pressure of 1000 psi in a semi-continuous mode.

Experiment 6

The process of Experiment 5 was repeated, except that different pressures, ranging from 75 psi to 1000 psi, were selected for the reactor, taking into consideration the compressibility factor. The rates of removal of H₂S by the SSII consortium obtained at the different pressures are tabulated below in Table 6.

TABLE 6

Rates Of Removal Of H ₂ S At Different Pressures	
Pressure, psi	H ₂ S removal rate, mmols/h
75	0.191
100	0.126
200	0.112
500	0.109
700	0.205
800	0.210
1000	0.325

The data demonstrate that at a higher pressure of 7500 psi, there is a direct relationship between pressure and the faster removal rate of H₂S, i.e. the higher the pressure, the higher is the removal of H₂S.

Experiment 7

The process of Experiment 5 was repeated except that in this experiment, the cell mass (wet weight of cells/600 ml of the culture medium) was varied in the range of 0.35% to 10%. In each of these runs, the initial pH of the culture medium was 7.5, and the pressure was 1,000 psi. The rates of H₂S removal under these conditions are graphically presented in FIGS. 4 and 5. This data indicates that the higher the cell density, the higher the removal rate of H₂S.

Experiment 8

The process of Experiment 7 was repeated, except that in this experiment, the cell masses of 0.35% and 5% were compared at an initial H₂S concentration of 200 ppm in a semi-continuous mode, and the gas inlet flow 10 times higher than the previously determined ratio of 1:1.6 between the reactor working volume verses the gas flow rate per hour, which for a 600 milliliter culture volume will be 0.96 liters per hour. Thus, the inlet flow rate of sour natural gas in this experiment was 9.6L/h. The data on outlet H₂S concentration is presented in FIG. 6. This data indicates that the contact time is reduced by two orders of magnitude (300 to 3 mins.) at 10 times the flow rate.

Experiment 9

The process of Experiment 1 was repeated, using the reactor illustrated in FIG. 1, except that alternative sources of organic nitrogen were substituted for the Sheftone-T™ suspension. The alternative sources of nitrogen used were Hoffman's dried blood (a commercially available source of organic nitrogen), Cargill 200/20 (an organic source of nitrogen available from Cargill Corp.), and different lots of chicken manure collected at different times from a local poultry farm. Each alternative nitrogen source was added in an amount to give the same organic nitrogen equivalent as provided by adding 5 milliliters of 10% Sheftone-T™ suspension. In each of these runs, the initial pH of the culture

medium was 7.5 and the cell concentration was 10% (wet weight of cells/1000 ml of culture broth). The initial H₂S concentration was 10,000 ppm. The rates of removal of H₂S under these conditions, or conversely the remaining H₂S in the outlet gas are graphically illustrated in FIGS. 7 and 8. The data indicates that the highest and most consistent H₂S removal was obtained when Cargill 200/20 was the source of organic nitrogen. This is also the most economical organic nitrogen source with a consistent nitrogen content.

In addition to the alternative organic nitrogen sources utilized in this example, other organic nitrogen sources, such as solubilized sewage sludge, and deactivated animal and/or poultry manure, could also be utilized.

Experiment 10

The process of Experiment 9 was repeated except that the process was carried out in the pressure reactor system of FIG. 3 and the organic sources of nitrogen were Cargill 200/20 and a combination of Sheftone-T™ and chicken manure. Each alternative nitrogen source was added in an amount to give the same organic nitrogen equivalent as provided by adding 5 milliliters of 10% Sheftone-T™ suspension. In each of the runs, the initial pH of the culture medium was 7.5 and the cell concentration was 10% (wet weight of cells/600 ml of culture broth). The initial H₂S concentration was 10,000 ppm. The rates of removal of H₂S under these conditions are illustrated in FIG. 9. The data indicates that, although each of the organic nitrogen sources are effective in the desulfurization process, the highest rate of H₂S removal was again obtained when Cargill 200/20 was the source of organic nitrogen.

Experiment 11

The process of Experiment 5 was repeated, except that the process was conducted at different temperatures ranging from 50° F. (10° C.) to 140° F. (60° C.) and the initial H₂S concentration in the gas was 10,000 ppm. The rates of removal of H₂S by the SSII consortium obtained at the different temperatures, while maintaining a pressure of 1000 psi, are graphically illustrated in FIG. 10. As FIG. 10 shows, higher rates of removal of H₂S are achieved at both elevated temperatures and pressures.

Experiment 12

The process of Experiment 11 was repeated, except that removal of CO₂ was monitored rather than removal of H₂S. The inlet sour natural gas contained 10.1% CO₂. Sixty gram wet weight SSII (10%) was suspended in 600 milliliters of medium, described in Table 1, containing 0.2% (weight/volume of medium) Cargill 200/20. The data is presented in FIG. 11. This data shows that the removal rates of CO₂ remains about the same up to a temperature of 104° F., but increases thereafter and at 140° F. is 0.616 lb/ft³ per hour.

We claim:

1. A process for the anaerobic removal of sulfur containing compounds from a gas stream comprising the steps of:
 - charging a reactor vessel with a microbial consortium of chemoautotrophic bacteria;
 - maintaining the reactor vessel at a temperature range of between about 77 degrees F. and about 140 degrees F.;
 - pressurizing said reactor with a malodorous gas stream containing the sulfur containing compounds to a pressure of between about 75 psi to about 1000 psi wherein sulfide in the gas stream is oxidized to elemental sulfur by the microbial consortium.
2. A process according to claim 1, wherein the reactor vessel is maintained at a temperature range of between about 100° F. and about 140° F.
3. A process according to claim 1, wherein the concentration of hydrogen sulfide in the gas stream containing the sulfur containing compounds is up to about 10,000 ppm.
4. A process according to claim 1, wherein the microbial consortium of chemoautotrophic bacteria charged into the reactor vessel has a wet cell mass of from about 0.35% to about 10.0% biomass.
5. The process according to claim 1, wherein an organic source of nitrogen is charged into the reactor prior or pressurization.
6. The process according to claim 1, wherein the gas stream includes at least one sulfide from the group consisting of hydrogen sulfide, methyl mercaptan, ethyl mercaptan, dimethyl mercaptan, carbon disulfide, and mixtures thereof.

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